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CERTAIN LAWS OF PHOTOCHEMICAL DECOMPOSITION OF OZONE IN THE LIQUID PHASE

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ABSTRACT

The photochemical decomposition of ozone in the liquid phase has been investigated at -183°C. For comparison, measurements have also been made of the reaction in the gaseous phase.

The quantum yield in the liquid phase -183°C, attains a value of 25; in the gaseous phase at room temperature it is about 3.5. Dilution of the liquid ozone with oxygen lowers the quantum yield. The value of the yield shows that the photochemical decomposition of ozone in the liquid phase proceeds according to a chain mechanism with the participation of excited oxygen molecules. The difference in the quantum yield values of the reaction in the liquid and gaseous phases may be explained in that in the liquid phase the conditions are evidentl~ more favorable for the transfer of energy fr(|the excited oxygen to the ozone molecules.

The object of the present article is to explain the role of the chains in the photochemical decomposition of ozone. /1605*

Investigations of the photochemical decomposition of ozone in the gaseous phase (Ref. 1, 3-10) show that the quantum yield of the reaction amounts to 3-6. This can occur if the reaction proceeds by means of short chains. The development of chains in this process is possible only at the expense of oxygen molecules possessing an excess amount of energy, i.e., the chains have to be energetic. In the absence of chains, the quantum yield of the reaction cannot be greater than 2, in accordance with the two stages of the reaction:

$$O_3 \xrightarrow{h\nu} O_2 + O,$$
$$O + O_3 = 2O_2.$$

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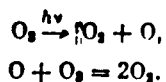
* Numbers given in the margin indicate pagination in the original foreign text.

However, the fact that the quantum yields only slightly exceed 2 creates, nevertheless, some uncertainty as to the role of the chain mechanism in this reaction.

To clarify the problem in question, we have investigated certain laws in the photochemical decomposition of ozone in the liquid phase. Apparently, the conditions which are created in an associated liquid are more conducive to the exchange of excitation energy between molecules than are those created in a gas.

As has been shown by S. Ya. Pshezhetskiy, I. A. Myasnikov, and N. A. Buneyev (Ref. 2), the reaction by which ozone is formed under the influence of fast electrons on oxygen proceeds much more effectively in the liquid phase than in the gaseous one. This is evidently related to the relatively greater participation of excited oxygen molecules in the reaction.

For purposes of comparison, we have also performed some measurements in the gaseous phase.

EXPERIMENTAL SECTION

Experiment Procedure. Since the number of molecules increases in the decomposition of ozone, the reaction is accompanied by an increase in the volume of the liquid if the oxygen remains in solution. On this basis, the dilatometric technique has been chosen for our measurements.

A quartz photechemical cell formed a parallepiped with a distance of 1 mm between the irradiated walls. The cell was soldered together with a calibrated capillary. The amount of the ozone condensed in the cell was such as to fill a part of the capillary. The reaction rate was determined from the rise in the level of the ozone in the capillary; the measurements were conducted by means of a horizontal microscope. The oxygen which was formed always remained in solution, since the volume of the gaseous phase did not oxceed ~ 0.04 cm^3.

The cell with the liquid ozone was immersed in a quartz Dewar vessel with parallel walls, filled with liquid oxygen.

A scheme of the arrangement is shown in Figure 1. Ozone, obtained from the electrolytic oxygen in the ozonizers, was condensed in the collector 3, which was cooled by liquid oxygen. The pressure of the ozone in this device was measured by means of a glass, spoon-like manometer (null instrument).
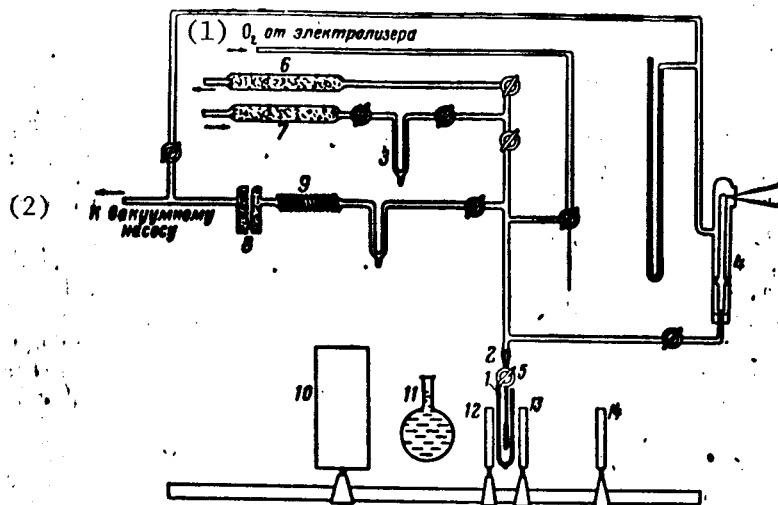
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Figure 1

Schematic of the Device

1 - Photochemical cell; 2 - ground-glass joint;
3 - trap for ozone condensation; 4 - glass mano-
meter; 5 - stopcock; 6,7 - tubes with phosphorous
anhydride; 8 - tubes with sodium hydroxide; 9 -
oven; 10 - mercury-vapor lamp; 11 - flask with
a solution of light filter; 12 - diaphragm; 13
and 14 - thermopile and photocell.

(1) O_2 from electrolyzer (electrolytic cell);
(2) to a vacuum pump

After evacuation, ozone evaporated into the device, where its
pressure was measured, and subsequently condensed in the photochemical
cell 1. After the condensation, the quartz stopcock 5, separating the
cell from the rest of the device, was closed. The unoccupied volume in
the capillary 1 was 0.04 cm^3.

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The stopcocks were lubricated with fluorinated hydrocarbons, which
do not react at room temperature with ozone.

Part of the experiments were conducted in an entirely soldered
quartz device, not containing any stopcocks (Figure 2). The ozone was
subsequently distilled in the collectors 1,2,3,4,6. The device was
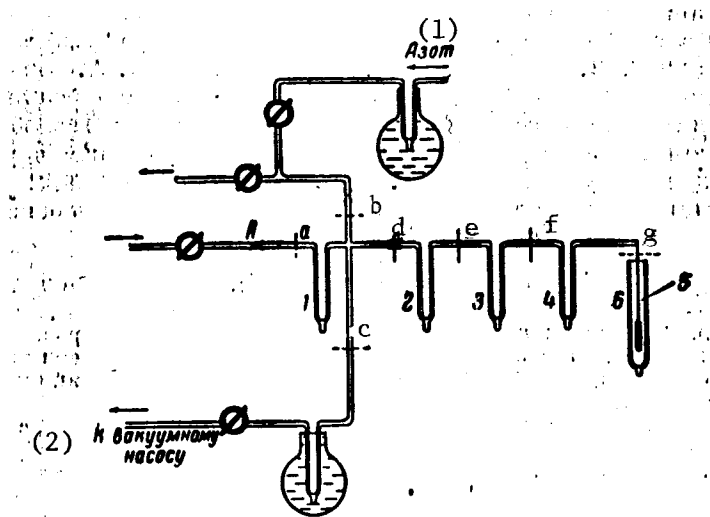sealed off at the locations denoted by letters.

Figure 2

Schematic of the Entirely Soldered Quartz Device

1,2,3,4, - collectors for the condensation
of ozone; 5 - photochemical cell; 6 - quartz
Dewar vessel, a,b,c,d,e,f,g - positions where
the sealing off process takes place.

(1) nitrogen
(2) to a vacuum pump

A PRK-2 mercury lamp served as a light source. A solution of
cobalt ⊝ and nickel sulfates was used as a light filter, which trans-
mits the mercury-vapor lamp lines 2967, 2804, 2652, 2537, and 2483 Å.
The average value of a quantum was equal to 106.58 kcal/mole (with an
error of about 10%).

The measurement of (the intensity of) light was performed by
means of a FESS-U 10 photocell, which was calibrated in the spectral
region employed by means of the thermopile. The thermopile itself was
calibrated according to a Hefner lamp with amyl acetate.

The intensity of the light absorbed by ozone was determined from
the difference between the readings of the galvanometer when measuring
the light which passed through a photochemical cell filled with ozone
and that which passed through the empty photochemical cell.

All experiments were conducted at a temperature of -183°C. The
quantity of decomposed ozone may be readily calculated from the increase

in the volume of the liquid, if the molar volumes of ozone and oxygen do not change with the concentration of the solution.

Special measurements have been compiled which show that for the investigated concentrations of solutions (from 97 to 74 molar percent of ozone), the deviations from additivity lie within the limits of experimental error. Therefore, the number of the ozone moles which have been decomposed may be determined from the following relation

$$m = \frac{\Delta V}{M} \frac{1}{1/\rho_{O_3} - 1/\rho_{O_2}},$$

where Δ, V are the increases in the volume of the liquid, and M and P are the molecular and specific weight, respectively.

The following values of the density (in g/cm^3) were used in the calculations: at $-183°C$ $\rho_{O_2} = 1.14$; $\rho_{O_3} = 1.57$ (Ref. 11).

Measurement Results. In order to determine the quantum yield of the decomposition of undiluted ($\sim 100\%$) liquid ozone, experiments were conducted in which the decomposition was no greater than 2%.

Table 1 presents the results of some experiments which have been performed using an entirely soldered quartz apparatus.

TABLE 1

$n = 0.67 \cdot 10^{-8}$ QUANTA/MOLE MINUTE

a	b	c	d
Time from start of the experiment, in minutes	Number of decomposed ozone moles $m \cdot 10^6$ per 10 min.	As a	As b
15	1.69	65	1.59
25	1.59	75	1.59
35	1.59	85	1.59
45	1.59	95	1.59
55	1.34		

The quantum yield $Y = \dfrac{1.59 \cdot 10^{-7}}{6.70 \cdot 10^{-9}} = 23.7$

Table 2 presents the results of the same experiments, but conducted by means of an apparatus containing stopcocks.

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TABLE 2

n = $3.4 \cdot 10^{-8}$ QUANTA/MOLE MINUTE

a	b	c	d
Time from start of the experiment, in minutes	Number of decomposed O_3 moles, $m \cdot 10^6$	As a	As b
5	6.03	35	4.68
10	4.60	40	4.72
15	4.43	45	4.32
20	3.39	50	4.34
25	4.23	55	4.17
30	4.27	60	4.34

$$\gamma = \frac{4,31 \cdot 10^{-6}}{3,4 \cdot 10^{-8} \cdot 5} = 25$$

As may be seen, the data obtained by means of the two devices agree satisfactorily with each other. /1608

Table 3 gives the results of one of the long experiments, in which a considerable change in the solution composition took place.

TABLE 3

n = $5.0 \cdot 10^{-8}$ QUANTA/MOLE MINUTE. INITIAL AMOUNT OF OZONE $2.91 \cdot 10^{-3}$ MOLES

Time from start of the experiment, in minutes	Number of decomposed moles $m \cdot 10^6$ per 5 min.	Molar fraction of ozone		
		$m' \cdot 10^4$	N_{O_2}	γ
5	9.66	7.74	0.960	----
20	6.71	5.39	0.958	26.9
35	6.22	4.97	0.940	24.8
55	6.55	5.25	0.922	26.2
70	5.27	4.20	0.912	21.0
90	5.80	4.63	0.906	23.2
115	4.45	4.40	0.900	22.0
150	5.64	4.51	0.884	22.6
170	5.18	4.16	0.875	20.7
195	5.49	4.40	0.865	22.0

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To obtain solutions with smaller ozone concentrations, a preliminary decomposition of ozone by unfiltered light from a mercury-vapor lamp was carried out in the photochemical cell. The data on the decomposition of ozone in such solutions are shown in Tables 4 and 5. The m' characterizes the decomposition, referred to a constant intensity of the absorbed energy, and was taken as $4 \cdot 10^{-8}$ quanta.

TABLE 4

INITIAL MOLAR FRACTION OF OZONE 0.805, n = $2.7 \cdot 10^{-8}$ QUANTA/MOLE MIN.

Time from start of experiment, in min.	Number of decomposed moles, $m \cdot 10^6$ per 5 min.	$m' \cdot 10^8$	γ
5	2.28	3.37	16.8
10	2.52	3.74	18.8
15	2.97	4.40	22.0
20	2.54	3.76	18.8
25	2.55	3.80	19.0
30	2.37	3.50	17.5
		Average	18.8

TABLE 5

INITIAL MOLAR FRACTION OF OZONE 0.715, n = $5.9 \cdot 10^{-8}$ QUANTA/MOLE MIN.

Time from start of experiment, in min.	$m \cdot 10^6$ per 5 min.	$m' \cdot 10^4$	γ
5	6.28	4.26	---
10	5.04	3.42	17.0
15	4.60	3.13	15.6
20	4.60	3.13	15.6
25	5.04	3.42	17.0
30	5.04	3.42	17.0
		Average	16.4

This relationship was due to a direct dependence between the decomposition and the radiation intensity, as will be clear from the following.

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Figure 3 represents the dependence of the quantum yield on the composition of the solution.
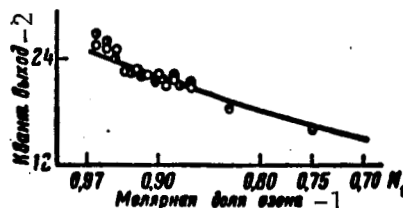

Figure 3

Dependence of the Quantum Yield of the Reaction in
the Liquid Phase on the Ozone Concentration

(1) Molar fraction of ozone;
(2) Quantum yield.

The dependence of the reaction rate on the intensity of the light absorbed by ozone (in quanta/mole min.) is represented in Figure 4. As is clear from the graph, the rate of the reaction is directly proportional to the intensity of light (the intensity of the absorbed light being changed by a factor of 7.5). The quantum yield of the reaction does not depend on the intensity of light.

Decomposition of Ozone in the Gaseous Phase. For purposes of comparison, the decomposition of ozone in the gaseous phase was measured in the same quartz apparatus, but with a different photochemical cell. The measurements were conducted on the basis of the increase in gas pressure at 20°C, determined by a glass manometer.

The initial gas pressure was equal to 415 mm Hg. Ozone contained about 3% oxygen. The results of the measurements are represented in Figure 5.

The experiments were conducted with interruptions. During this time, the adsorption of ozone on the walls of the vessel was taking place. This was manifested in the pressure jump at the initial moment after the lamp had been switched on, and was apparently due to the desorption of ozone when the light was turned on. It may have possibly been caused by a more intensive decomposition of ozone in the adsorption layer.
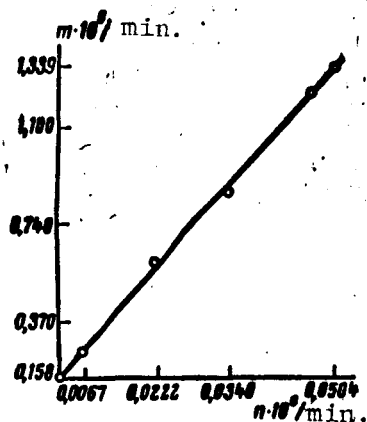
Figure 4

Dependence of the Reaction Rate on the Intensity of the Absorbed Light.

Ordinate: number of moles of ozone being
decomposed per one minute.
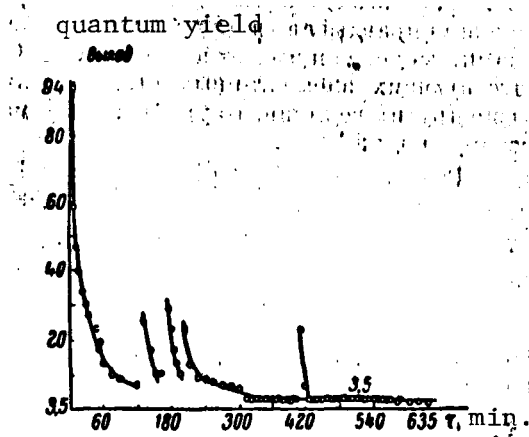Abscissa: number of light quanta per one minute.

Figure 5

Dependence of the Quantum Yield of Ozone Decomposition
in the Gaseous Phase on Time.

As time elapses, the process acquires a regular character (length
of time interval: 300-600 min.). Under the conditions of a regular

process with 25% of ozone in the gas, the quantum yield is on the average 3.5. According to the data of Schumacher (Ref. 4,5), the quantum yield at such concentrations is on the average equal to 2.0; according to the data of Heidt (Ref. 9) it is equal to 3.0.

Discussion of the Results

The value of the quantum yield of the reaction, which equals 25, shows that the decomposition of ozone in the liquid phase represents a valuable process.

The data on the dependence of the rate and the decomposition quantum yield on the composition of the ozone-oxygen solution indicate that oxygen inhibits the reaction. Figure 6 shows the dependence of the photodecomposition quantum yield on the ozone concentration in the liquid and gaseous phases [the latter according to Schumacher (Ref. 5.)]

It is clear from the graph that in the liquid phase, oxygen inhibits the reaction more strongly than when it is in the gaseous phase.
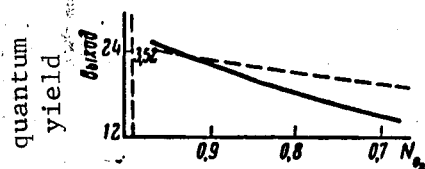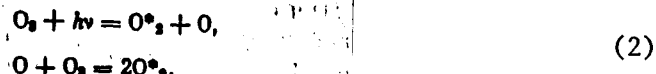

Figure 6

Dependence of the Quantum Yield on the Molar Fraction of Ozone.

Solid line represents the reaction in the liquid phase; dotted line represents the reaction in the gaseous phase 5.

The mechanism for the photochemical decomposition of ozone can be represented by the following scheme:

$$O_3 + h\nu = O^*_2 + O, \quad \text{(1)}$$

$$O + O_3 = 2O^*_2, \quad \text{(2)}$$

$$O + O_3 + O_3 = O_3 + O_3, \quad \text{(3)}$$

$$O^*_2 + O_3 = O_2 + O_2 + O, \quad \text{(4)}$$

$$O^*_2 + O_3 = O_2 + O_3, \quad \text{(5)}$$

$$O^*_2 + O_2 = O_2 + O_2. \quad \text{(6)}$$

The equation for the rate of the photochemical reaction, corresponding to this scheme, was derived by Schumacher using the method of stationary concentrations, and is well substantiated for a reaction in the gaseous phase (Ref. 5). If one neglects the terms, containing the ratio $k_3/k2[O2]$ (k is the rate constant of the corresponding elementary stages), which are less than the other terms by several orders of magnitude, then the equation of Schumacher is reduced to the following simple form:

$$-\frac{d[O_3]}{dt} = I \frac{a\,[O_3] + b\,[O_2]}{c\,[O_3] + b\,[O_2]}, \quad \text{(1)}$$

where I is the light intensity,

$$a = 4 + 2\frac{k_5}{k_4}, \qquad b = \frac{k_6}{k_4}, \qquad c = \frac{k_5}{k_4} - 1.$$

The curve in Figure 3 was calculated from Equation 1.

The observed discrepancies in the laws of the decomposition reaction of ozone in the liquid and gaseous phases should be attributed to a different effectiveness of certain elementary stages. A greater value of the reaction quantum yield in the liquid, as compared with the gas, is apparently connected with the fact that in the liquid conditions are created which are more favorable to the exchange of excitation energy from oxygen molecules to ozone molecules.

A slightly greater inhibiting action of oxygen in the liquid phase may be due to a greater effectiveness of reaction 3, because of the effect of "local" collisions (Ref. 12), and a greater number of triple collisions

in a liquid as compared with a gas. The small quantum yield for ozone decomposition in the gaseous phase must be related to the fact that in the thermal decomposition of ozone, chains do not appear to any noticeable extent, and the kinetics of the reaction can be interpreted without introducing the concept of a chain mechanism.

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Conclusions

1. The quantum yield of the photochemical decomposition reaction of liquid ozone under the action of ultraviolet light has been measured. The quantum yield in the liquid phase at -183°C attains the value of 25; dilution of liquid ozone with oxygen lowers the quantum yield.

2. The quantum yield of the reaction shows that the photochemical decomposition of ozone in the liquid phase proceeds according to a chain mechanism, with the participation of excited oxygen molecules.

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